

Supporting Information

Catalytic Performance and Mechanism Study of the Isomerization of 2,5-Dichlorotoluene to 2,4- Dichlorotoluene

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Experimental Section

Characterization

X-ray diffraction (XRD) measurements were performed on a SmartLab 9 kW X-ray powder diffractometer (RIGAKU, Japan) using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) and a nickel monochromator (0.6 mm), with a scanning speed of $10^\circ \text{ min}^{-1}$ and a scanning range from 5° to 60° .

Fourier transform infrared (FT-IR) spectroscopy was conducted using a Thermo Fisher IS 10 spectrometer. After drying the samples for 24 hours, they were mixed with KBr, and the spectrum was recorded in the range of $4000\text{-}500 \text{ cm}^{-1}$ with a resolution of 4 cm^{-1} .

Nitrogen adsorption-desorption measurements of the catalysts were carried out using a BET surface area and pore size analyzer (3H-2000PM2) from Beijing Best Instrument Science and Technology Co., Ltd. The samples were pretreated under vacuum at 200°C for 4 hours, and the measurements were performed at liquid nitrogen temperature (-196°C). Pore size distribution analysis was conducted using the BJH method. The BET method was employed to calculate the specific surface area. The pore volume and surface area were measured by the t-Plot method.

Ammonia temperature-programmed desorption (NH_3 -TPD) experiments were conducted using a TP-5080-B multipurpose adsorption instrument from Tianjin Xianquan Co. Ltd. Approximately 0.3 g of the sample was purged with high-purity nitrogen gas at 450°C for 1 hour, then cooled to 100°C before exposure to NH_3 gas for 1 hour to achieve adsorption saturation. Subsequently, the sample was heated from 100°C to 800°C at a rate of $10^\circ\text{C}/\text{min}$ in an ammonia gas flow, and the desorbed NH_3 was detected by a thermal conductivity detector, allowing the construction of the desorption curve.

Infrared spectra were recorded using a TENSOR 27 FT-IR spectrometer from Bruker (Germany). Approximately 10 mg of powder samples were compressed into pellets. The samples underwent an activation process before adsorption, involving heating to 350°C and vacuum purification for 2 hours. Subsequently, they were cooled to room temperature. After adsorbing pyridine at room temperature, the samples were heated to the desired temperature for 30 minutes under vacuum. Infrared spectra in the wavenumber range of $1700\text{-}1400 \text{ cm}^{-1}$ were recorded. Spectra of the samples were recorded at 150°C and 350°C .

Solid-state ^{27}Al nuclear magnetic resonance (NMR) characterizations of the samples were conducted using a Bruker Avance III 600 MHz NMR spectrometer (Germany). The measurements were made with a magnetic field strength of 14.2 T and a spinning speed of 12 kHz. A single-pulse sequence was used with a relaxation time of 1 s. Aluminum nitrate aqueous solution was employed as the reference sample for chemical shift calibration.

X-ray photoelectron spectroscopy (XPS) data were obtained using a VersaProbe III electron spectrometer. The instrument had a resolution of 0.2%. Al was used as the X-ray source, with an X-ray irradiation energy of 1486.6 eV. The tests were carried out under vacuum conditions. Standard carbon spectrum binding energy (284.8 eV) was utilized to correct the electron binding energy of the analyzed elements.

Material morphology characterization was performed using a field emission scanning electron microscope (FE-SEM), JEOL-S4800 model (HITACHI, Japan), with an operating voltage of 5 kV.

Table S1 Effect of hydrothermal temperature on the isomerization of 2, 5-dichlorotoluene

Catalyst	2, 5-DCT Conversion (%)	Selectivity (%)							
		2, 4-DCT	3, 4-DCT	BZ	TL	MX	BC	CBZ	Others
HZ	29.2	66.4	12.7	5.6	4.0	3.2	4.2	2.0	1.9
HZ-300	27.1	62.9	12.3	4.8	2.7	1.2	5.2	3.1	7.8
HZ-400	17.7	78.7	14.6	0.8	0.2	0.0	3.6	0.7	1.4
HZ-500	6.9	69.8	12.5	1.5	1.0	0.7	2.0	7.6	4.9

2, 5-DCT is 2, 5-Dichlorotoluene, 2, 4-DCT is 2, 4-Dichlorotoluene, 3, 4-DCT is 3, 4-Dichlorotoluene, BZ is Benzene, TL is Toluene, MX is Xylene, BC is Chlorotoluene, CBZ is Chloroethylbenzene.

Table S2 Effect of LHSV on isomerization of 2,5-dichlorotoluene

LHSV h ⁻¹	2, 5-DCT Conversion (%)	Selectivity (%)							
		2, 4-DCT	3, 4-DCT	BZ	TL	MX	BC	CBZ	Others
0.4	35.5	60.9	11.4	5.1	3.0	0.9	8.7	1.4	8.6
0.6	30.6	64.9	12.1	5.7	4.0	2.1	5.4	2.6	3.2
0.8	17.7	78.7	14.6	0.8	0.2	0.0	3.6	0.7	1.4

Calculation details

All calculations in this study were performed using Gaussian 16. The structural optimization and frequency calculations were carried out using the B3PYP/6-31G** method, while the single-point energy calculations utilized the B3PYP/def2tzvp method. In both the structural optimization and single-point energy calculations, the third-generation dispersion correction method proposed by Grimme was applied to correct the errors associated with the B3LYP method when dealing with weak interactions. Due to the large number of atoms in the HZSM-5 zeolite system, a local atomic structure of the catalytic active center was extracted while fixing the distances of reactants that are far apart and have a minimal impact on the reaction, without compromising the accuracy and precision of the results. This was done to simulate the bulk-phase environment. The truncation accuracy for structural optimization was set at $1e^{-6}$ eV/atom. Separate basis sets were used for heavy atoms and hydrogen atoms. Grid integration precision was set to ultrafine, and the energy calculation truncation was set to $1e^{-7}$ eV/atom.

The process of catalyst-catalyzed conversion of reactants into products is controlled by both thermodynamics and kinetics. Thermodynamics determine whether the reaction is theoretically possible, while the energy barrier of the reaction is governed by kinetic processes. Therefore, kinetic calculations for isomerization reactions were performed to investigate the isomerization mechanism and the role of acid centers throughout the entire process. The transition state search was conducted using the TS method, and the initial guess for atomic displacements used the Berny method. The calcfc keyword was employed to precisely calculate the Hessian matrix of the initial structure, and no eigenvalue number check was performed during the optimization process. The transition state search results were judged by the presence of one and only one imaginary frequency, pointing towards the final state structure. Additionally, the Intrinsic Reaction Coordinate (IRC) analysis was carried out to validate the obtained transition state structure, with a step size set to 10.

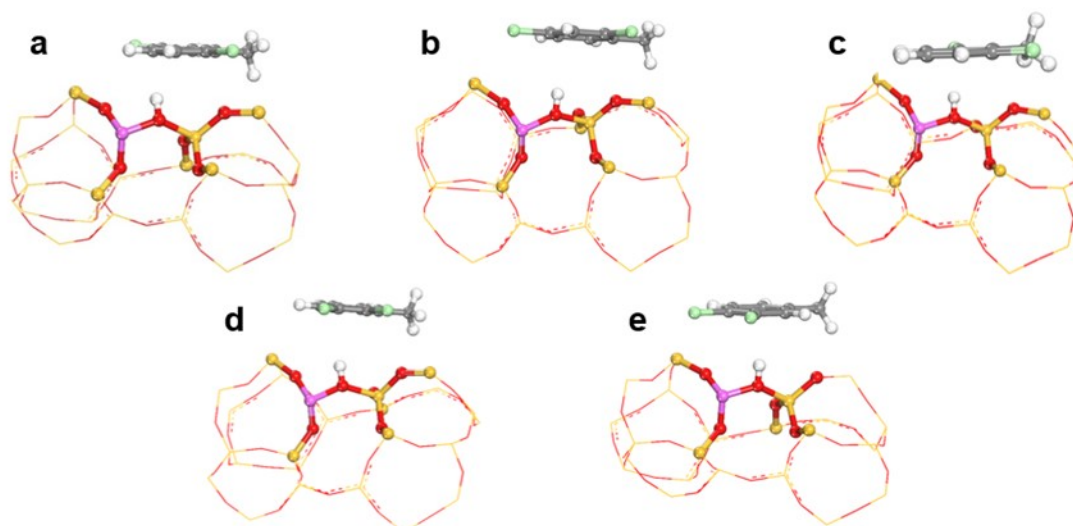


Fig. S1 Initial configuration of product and reactant adsorption on the surface of HZSM-5: (a) 2, 5-DCT, (b) 2, 4-DCT, (c) 2, 6-DCT, (e) 2, 3-DCT, (f) 3, 4-DCT

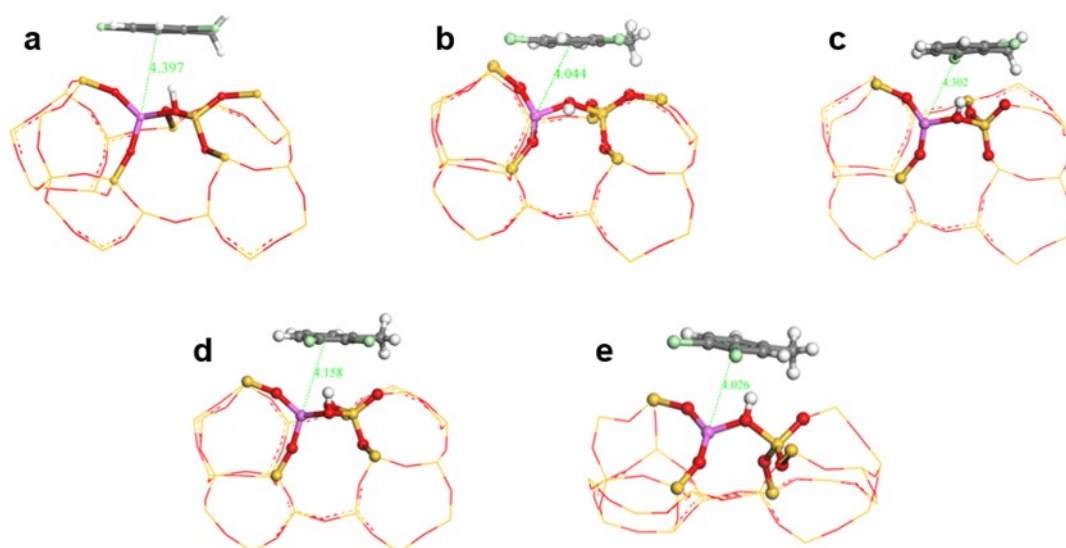


Fig. S2 Conformation of the reactants and products after optimization of adsorption structure on surface of HZSM-5: (a) 2, 5-DCT, (b) 2, 4-DCT, (c) 2, 6-DCT, (e) 2, 3-DCT, (f) 3, 4-DCT

Table S3 Comparison of methods

	method	Material	catalyst	Main product distribution
				2, 6-DCT selectivity is 37.7%
Industrial Applications	Chloride reaction	Chlorotoluene	Metal chloride	2, 5-DCT selectivity is 28.2%
				2, 4-DCT selectivity is 16.9%
Experimental Research	Gas phase isomerization	2, 5-DCT	Acid molecular sieve	2, 4-DCT selectivity is 78.7%